SYNTHESIS AND CHARACTERIZATION OF POLYMER GEL ELECTROLYTE

Thesis Submitted for the Award of the Degree of

Master of Science

By

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DECLARATION

I hereby declare that the work carried out in this thesis is entirely original. It was carried out by me along with Miss Paradarsini Parida and Miss Swagatika Bhoi at Department of Physics, National Institute of Technology, Rourkela. I further declare that it has not formed the basis for the award of any degree, diploma, or similar title of any university or institution.

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CERTIFICATE

This is to certify that the thesis entitled "**Synthesis and Characterization of Polymer gel Electrolytes**" being submitted by **MANORANJAN SAMAL** in partial fulfilment of the requirements for the award of the degree of Master of Science in Physics at National Institute of Technology, Rourkela is an authentic experimental work carried out by him under our supervision. To the best of our knowledge, the experimental matter embodied in the thesis has not been submitted to any other University/Institute for the award of any degree or diploma.

Date:

Dr. Dillip Kumar Pradhan

Dr. Sidhartha Jena

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I express my gratitude to my parents and my sister without the help of whom the present work would not have been a success.

ABSTRACT

Polymer gel electrolytes were prepared by the gelation method having different O/Na ratio (O/Na = 20, 40, 60, 80, 100) taking PVdF as polymer host, sodium iodide as salt and DMF as solvent. After synthesis it is characterized with different experimental techniques. The structural and morphological characterization was done by x-ray diffraction and scanning electron microscope analysis. Similarly electrical property was studied by impedance spectroscopy. From XRD we found about crystallinity and amorphous nature of polymer gel electrolyte and from impedance spectroscopy we measured bulk resistance, dc conductivity, and other related dielectric parameters.

Contents **PAGE NO**

CHAPTER-1

1.1. Electrolyte 1

1.2. Why we need solid electrolyte 1

1.3. Classification of solid electrolyte 2

1.4. Classification of polymer electrolyte 2

1.5. Gel and polymer gel electrolyte 3

1.6. Role of polymer salt and solvent in PGE 3

1.7. Transport mechanism in ionic and super ionic solid 4

1.8. Application 5

1.9. Disadvantages 5

1.10. Literature survey 6

1.11. Objectives 7

1.12. Organisation of thesis 7

CHAPTER -2

2.1. Synthesis 8

2.2. Characterization 11

CHAPTER-3

Results and discussion 13-20

CHAPTER-4

Summary and conclusion 21

References 22-23

INTRODUCTION

1.1. Electrolyte

Electrolyte is any substance which contains free ions that make the substance electrically conductivity. Generally electrolyte is formed when a solute is dissolved in a suitable solvent. e.g., $ZnCl_2 + HCl \rightarrow Zn^{+} + 2Cl^{-1}$, when $ZnCl_2$ is dissolved in HCl it gives Zn^{+} and $2Cl^{-}$ [1].

Depending upon the state of electrolytes there are two types: (i) liquid electrolyte and (ii) solid electrolyte. The electrolyte which is in liquid state is called liquid electrolyte. E.g. when NaCl is dissolved in water it gives Na^{+} and Cl^{-}. The conductivity of liquid electrolyte is very high of the order of 10^{-1}S/cm. The electrolyte which is in solid state is called solid electrolyte. They are also called as super ionic or fast ionic conductors, which exhibit an exceptionally high ionic conduction at room temperature. The ionic conductivity of electrolyte vary from10^{-2} to 10^{-6} Scm^{-1}. For example: Yattria stabilized Zirconia

1.2.Why we need solid electrolyte

Still now, majority electrochemical and electrohromic devices are liquid-aqueous electrolyte based devices. These devices were suffering a lot of disadvantages which are given below:

Limited temperature range of operation: We can't use the liquid electrolyte for a wide temperature range because normally below 0^{0} **C** and above 100^{0}C, liquid electrolytes cease to work.

Corrosion of electrolyte: when liquid electrolyte is used in battery after operation of so many cycles there is deposition of uneven chemicals at the electrodes-electrolyte interface, which damage the battery

Internal short circuiting: In liquid electrolyte there may happen internal short circuiting due to pressing of electrolyte.

Leakage of electrolyte: Since electrolyte is in liquid state there is a chance of leakage of electrolyte.

Bulky in size and low energy density: Due to large size of the liquid electrolyte it takes more space with low power and energy density.

1.3. Classification of solid electrolyte

Depending upon the different microstructure and physical properties; solid electrolyte are divided into following categories. These are (i) Framework crystalline material, (ii) Amorphous-glassy electrolytes, (iii) Composite electrolyte (iv) Polymer electrolytes. Out of these four types of solid electrolyte first one is ordered whereas the rest are disordered. Amorphous glassy and polymer electrolytes are microscopically disordered, whereas composite electrolytes are macroscopically disordered [2].

Now we are going to discuss about the polymer electrolyte, which is the scope of the thesis:

Polymer electrolyte

Polymer electrolytes are usually formed by comlexing polar polymers like PEO, PPO, PEG etc with ionic salts of monovalent alkali metal or divalent transition metal ammonium salts [2, 3]. Polymer electrolytes are mostly prepared either by solution cast method or electro-deposition method. Polymer electrolytes have several advantages over liquid electrolyte such as free from leakage, good processibility, design flexibility, space casing, light weight, and possibility of high energy and power density [2, 4].

For the purpose of application in solid electrochemical device, the polymer electrolyte should possess the following properties [2, 5, 6, 7]: (i) high ionic conductivity and high transference number; (ii) high chemical, thermal and thermal stabilities and (iii) good compatibility with the electrode.

1.4. Classification of polymer electrolyte

Depending upon the procedure adopted to prepare polymer electrolyte for desired level of conductivity, polymer electrolytes can be classified in to following categories:

- **Conventional polymer salt complex or dry SPE**

  Dry SPE's are prepared by dissolving ionic salts into polar polymer hosts, namely polyethylene oxide (PEO) and poly propylene oxide (PPO). The casting of film is done either by solution cast method, electro deposition method or sol gel method.

- **Plasticized polymer salt complex**

  They are prepared by adding liquid plasticizers into dry SPEs. Plasticized polymer salt complex possesses both liquid and solid like behaviour. By this process ambient conductivity gets substantially enhanced, but deterioration takes place in the mechanical stability and corrosive reactivity of polymer electrolyte also increased.

- **Polymer gel electrolyte (PGE)**

  Polymer gel electrolyte is usually obtained by adding polymer into solution of liquid plasticizer and salt. Polymer electrolyte has also disadvantages as mentioned for the plasticized polymer electrolytes. Later we will discuss more about PGE.

- **Composite polymer electrolyte (CPE)**

  CPEs are basically analogues to phase composite solid electrolyte systems. They are also prepared simply by dispersing a small fraction of micro/nano size inorganic or organic filler particles into the conventional SPE host. SPE act as phase-1, while fillers as phase-II dispersed. As a result the ionic conductivity, the mechanical stability and the interfacial activity of usually get enhanced substantially.

1.5. Gel and Polymer gel electrolyte

Gels are the three dimensional network structures of polymer and their swollen mattes. They possess both the cohesive properties of solids and the diffusive transport properties of liquid. Their properties vary from viscous liquid to hard solid according to chemical composition [8].

The properties of polymer gel electrolyte have been found to depend upon the structure of the polymer network that makes up the gel as well as on the interaction of the network and the solvent. As the polymer networks are solvated by a large amount of the trapped solvent so gels generally possess high mobility [8]. The polymer gel electrolyte is usually formed by adding the polymer in to solvent-salt solution.

1.6. Role of polymer, salt and solvent in PGE

In polymer gel electrolytes the salt generally provides free/mobile ions which take part in the conduction process and the solvent helps in solvating the salt and also acts as a conducting medium whereas the polymer is reported to provide mechanical stability by increasing the viscosity of electrolyte. The salt used should generally have large anions and low dissociation energy so that it easily dissociates. The salts should have also bulk anions. The solvent used should have high dielectric constant, low viscosity and high boiling point, low melting point and also low molecular weight. The polymer should have following properties: high molecular weight, low glass transition temperature [8].

Table-1 some organic salts commonly used as plasticizer

	Melting point(^{0}c)	Boiling Point(^{0}c)	Density G cm^{-3}	Dielectric constant
Ethylene carbonate	36.4	248	1.34	89.78
Propylene carbonate	-48.8	242	1.204	66.14
Dimethyl carbonate	2.4	90	1.06	3.12
Diethyl carbonate	-43.0	126	0.975	2.82

1.7. Transport mechanism in ionic and super ionic solids

Defects take part an essential role for the ionic conduction in polymer electrolyte or gel polymer electrolyte. Ionic conduction can be explained by two mechanisms either VTF equation or Arrhenius equation.

VTF equation

One group of polymer electrolytes obeys VTF type relation, expressed by the following equation

$$\sigma = AT^{-2}\exp[-E_a/(T-T_0)]$$

Where A is the pre-exponential factor and T_0 the equilibrium glass transition temperature. In VTF relation, conductivity is reciprocal of temp is typically non-linear which is indicative of a conductivity mechanism involving in hoping motion coupled with the relaxation /breathing or segmental motion.[9]

Arrhenius equation

On the other hand some polymer electrolytes obey Arrhenius equation for ion conduction mechanism, which is given by

$$\sigma = \sigma_0 \exp(-E_A/KT)$$

Where E_A is the activation energy can be calculated from the linear-least –square fit of the data from logσ versus 1/T curve. The material exhibiting linear Arrhenius equation indicates ion transport via simple hoping mechanism decoupled from the polymer chain breathing [9].

1.8. APPLICATION

polymer gel electrolyte are vastly used due to some of their unique properties like high value of conductivity at room temperature(10^{-2}-10^{-4} s/cm),ease of preparation, wide range of composition and hence wider control of properties ,good adhesive properties suitable for lamination, good thermal ,electrochemical stability etc. Polymer gel electrolytes are used in fuel cells, super capacitor, electro chromic display devices, sensors, high-low solid state batteries.

1.9. DISADVANTAGES

The presence of liquid plasticizers in excessive amount in gel electrolyte leads to a number of disadvantages commonly faced in liquid electrolyte. The other problem mainly Li^+ conducting gel electrolytes are used in the lithium battery has been the reactivity of the electrolyte with the lithium metal surface. The mechanical stability of the gel electrolytes is very poor [10].

1.10. LITERATURE SURVEY

S. Panero et. al. demonstrated the development of lithium ion conducting gel membranes and their use in advance-design, plastic-like electrochemical devices. Relevant example is membrane formed membranes by gelification of a $LiPF_6$ ethylene carbonate-dimethyl carbonate solution into a PAN. [10].

H.M Upadhaya , R.K. Yadav prepared few PMMA based Na^+ ion conducting gel electrolytes by blending the mixture of PMMA+PC and PMMA+(EC+PC) in appropriate ratio with varying $NaClO_4$ concentration. A ionic conductivity of the order of 10^{-3} Scm^{-1} have been obtained for O/Na ratio 10 and 40 respectively for two systems [11].

G.B. Appetecchi, P. ROMAGNOLI and B. Scrosati Prepared novel composite gel type polymer electrolyte by dispersing ceramic powder into a matrix formed by a lithium salt solution contained in a PAN matrix .They reported that these new types of composite gel electrolyte have high ionic

conductivity, wide electrochemical stability and particularly high chemical integrity even at temperature above ambient. [12]

Mario Wachtler et al studied on PVdF based SiO2 containing composite gel type polymer electrolytes for lithium batteries. The addition of SiO_2 filler affects mostly the structure of polymer matrix and doesn't affect the state of electrolyte [13]

V. Gentili et al worked to determine whether the dispersion of ceramic fillers have any promotion effect on the properties of solid like, gel type lithium conducting polymer electrolyte. They used different but complementary techniques like SEM analysis, voltammetry and impedance spectroscopy and demonstrated that dispersion of suitable ceramic fillers in solid like PVdF best gel polymer gel electrolyte give rise to composite GPE having some important specific properties. These fillers do not influence the transport properties of these composite GPE.[14]

T. Yamamoto, T.Hara, K.Segwa, K. Honda tested lithium ion polymer batteries with PVdF based gel electrolyte. The maximum discharge capacity was found to be520 Wh^{-1} They found that PVdF gel electrolyte not only high ionic conductivity but also entirely suppressed oxidation [15]

H. Nakagawa et. al. prepared ionic liquid $LiEMIBF_4$ by mixing 1-ethyl-3-methylimidazolium tetrafluoroborate ($EMIBF_4$) with $LiBF_4$. The ionic conductivity of $LiEMIBF_4$ was 7.4 $mScm^{-1}$ at room temperature. It has high thermal stability around 300°C. I has capacity retention 93.8% after 50 cycles was of the initial capacity in the $LiEMIBF_4$ cell. Discharge potential profile of the $GLiEMIBF_4$ cell showed debility possibly due to the concentration polarization in the gelled electrolyte.[16]

Thierry Michot, et. al. synthesized polymer gel electrolyte by taking PVdF as polymer, tetrahydrofuran (THF), and an electrolyte solution of 1 M $LiBF_4$ in propylene carbonate (PC). During the casting process, phase separation happened leading to non- or low-porous membranes.it has conductivity 10^{-3} S/cm at 30°C.

1.11. OBJECTIVES:

The followings are the main objectives of our project work

(i) Synthesis of polymer gel electrolyte by gelation method

(ii) Structural characterization of polymer electrolyte by X-ray diffraction technique

(iii) Micro structural characterization using Scanning Electron Microscope (SEM)

(iv) Studies of ion transport mechanism using Dielectric Spectroscopy.

1.12. ORGANIZATION THESIS:

Chapter-1 contains introduction part which includes types of electrolyte, why we need solid electrolyte, polymer electrolyte, gel polymer electrolyte, transport mechanism in polymer electrolyte, literature survey, and objectives.

Chapter-2 describes Synthesis and experimental technique. For synthesis we used gelation method and experimental techniques incudes XRD, SEM and dielectric spectroscopy.

Chapter-3 includes result and discussions

Chapter-4 contains summary and conclusion

CHAPTER -2

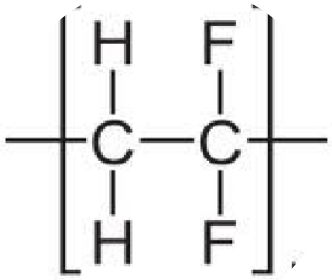
2.1. SYNTHESIS

Polymer electrolyte can be synthesized by various methods. Some of the methods for synthesis of polymer gel electrolyte are: solvent casting method, electro-deposition method and sol gel method. In present case we have used gelation method for preparation of polymer gel electrolyte.

Material under investigation

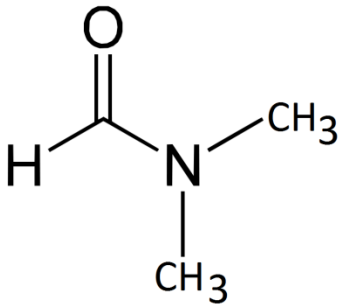
Polyvinylidene difluoride (PVdF)

For synthesis of polymer gel electrolyte we take Polyvinylidene difluoride (PVdF) as polymer. It has high molecular weight. Molecular weight of a single chain of PVdF is 64. It provides the mechanical stability to polymer gel electrolyte



Dimethyl formamide (DMF)

For synthesis of polymer gel electrolyte we take DMF as solvent. It has high dielectric constant, low viscosity and high boiling point. Molecular weight of DMF is 73.1.



Sodium iodide (NaI)

Generally sodium iodide provides free ions which just part in conduction which take part in conduction process. It has low lattice energy so that it easily dissociates into ions. It's molecular weight is 149.89.

2.1.1. GELATION METHOD

For synthesis of polymer-gel electrolyte, gelation method is one of the simplest methods. For the synthesis of polymer gel electrolyte we have used Dimethyl formamide (DMF) as solvent, sodium iodide (NaI) as salt and Polyvinylidene difluoride PVDF as polymer. This methods involves the following steps

2.1.2. PROCEDURE

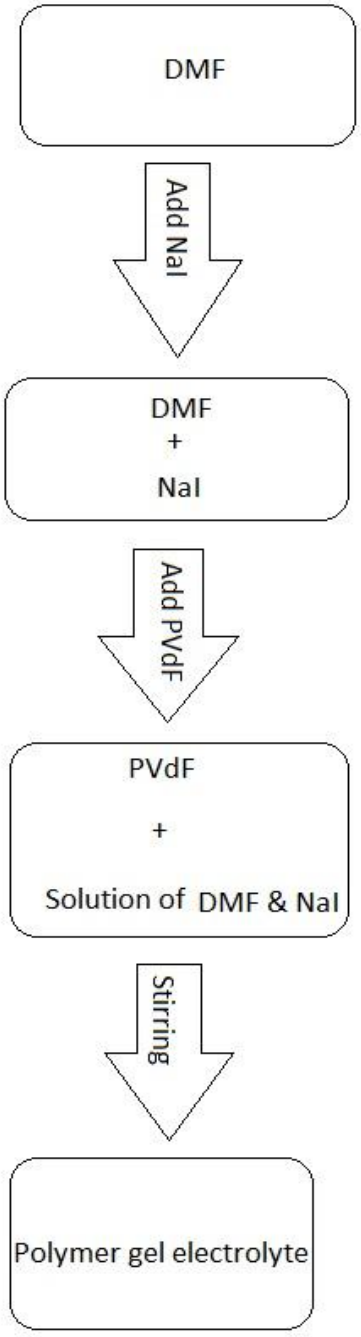
(a) 5ml of DMF (solvent) is taken in a beaker.

(b)Calculated amount of NaI salt is added to solvent for different O/Na ratio (O/Na= 20, 40, 60, 80, 100).

(c) First NaI is dissolving in the solvent. Then polymer is added in to the solution of polymer-solvent and stirred for some time and it casted on Petridis. Polymer and solvent ratio was maintained 1:3 throughout the study.

(d) Then the total solvent-Salt-Polymer solution is few days left for gelation.

2.1.3. FLOWCHART:



2.2CHARACTERIZATION

Materials properties like structure, surface morphology, electrical, thermal, mechanical, optical etc. should be studied in details in order to understand the chemistry and physics of materials. In the present case we have studied, the structural properties of polymer gel electrolyte using X-ray diffraction, surface morphology by scanning electron microscope and electrical properties using complex impedance analysis.

2.2.1. X-Ray Diffraction

X-ray diffraction (XRD) is a non-destructive technique which provides information about structural properties like phase analysis, lattice parameter, crystallinity etc. For XRD we use Bragg's law of diffraction:

$$2d\sin\Theta = n\lambda$$

Where d is the inter planner spacing, Θ is the angle of incidence, λ is wavelength of x-ray.

Using Phillips x-ray powder diffractometer with x-ray wavelength $1.5405A^0$, in a 2θ range ($10 \leq 2\theta \leq 40$) and at a scanning rate of 30/min we get XRD pattern of polymer gel electrolyte. From XRD data we can calculate interchain spacing and interplanar spacing.

2.2.2. SCANNING ELECTRON MICROSCOPE (SEM)

In scanning electron microscope, a beam of focused electrons scanned the object, the secondary electrons produced due to the interaction of electron and object being collected to form a three-dimensional image on a display screen. Using scanning electron microscope we can know about (i) shape, size and arrangement of the particles making up the object (ii) surface feature of an object or "how it looks", (iii) elements and compounds the sample is composed of can be studied using an electron microscope.

2.2.3. IMPEDANCE SPECTROSCOPY (IS)

It is a non-destructive technique which is used to study the electrical properties of material where the response of a system to an applied sinusoidally varying alternating voltage is recorded. The impedance spectroscopy was done by a computer controlled Impedance analyser ((PSM 1735 Impedance Analysis Package (Newton 4th Ltd.). Polymer gel electrolyte is sandwiched between two

stainless steel electrodes before taking measurement. The frequency dependence of various impedance parameters of a material can be described via the complex permittivity (ε^*),complex impedance (Z^*), complex electric modulus (M^*) and dielectric loss (tanδ). These are related to each other as follows:

Impedance (Z^*) = $Z^{'}$-$Z^{''}$, Permittivity (ε^*) = $1/jwC_0Z^* = \varepsilon' - \varepsilon''$, Modulus (m*) = $jwC_0Z^* = (\varepsilon^*)^{-1}$

AC conductivity(σ_{ac})=$\epsilon_0\varepsilon_r\omega tan\delta$

Using impedance spectroscopy we can study ionic transport, bulk conduction, grain boundary conduction, properties of the inter-granular and interfacial regions and interrelations, their temperature and frequency dependent phenomena, their interfaces with electronically conducting electrodes. We can also evaluate the relaxation frequency (ω_{max}) [18].

CHAPTER-3

RESULTS AND DISCUSIONS

3.1. X-RAY DIFFRACTION

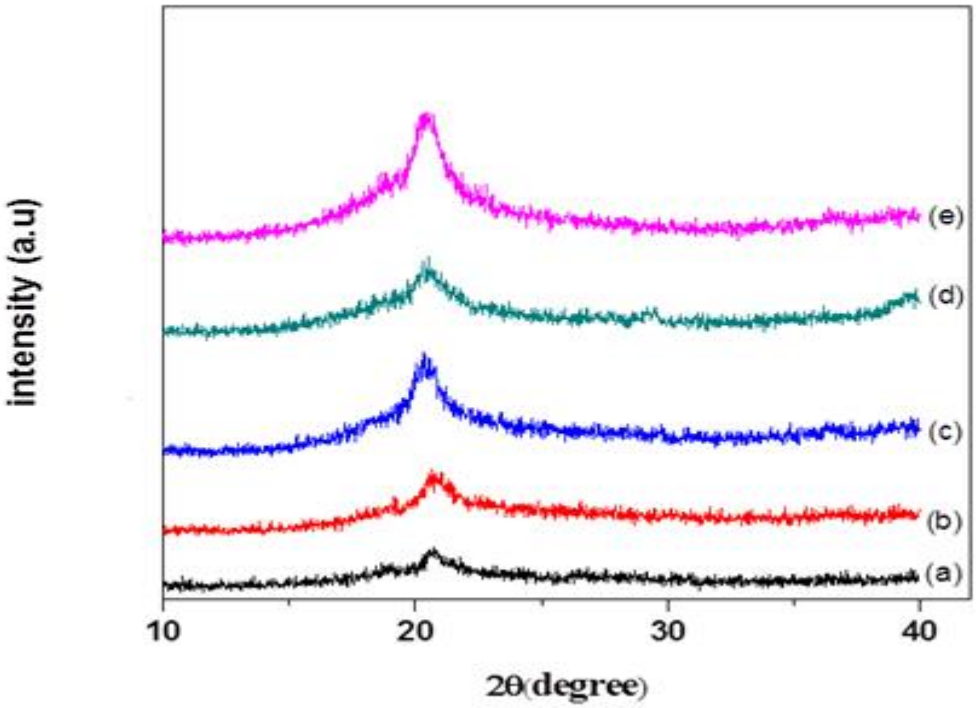


Fig-3.1 Room temperature XRD patterns PGE (a) O/Na=20, (b) O/Na=40 (c) 0/Na=60 (d) O/Na=80 (e) O/Na=100

Figure 3.1 shows the XRD patterns of PGEs with different O/Na ratio (i.e.,20, 40, 60, 80,100). From this figure, we observed a peak around 20^0 over amorphous hump irrespective of different concentration. This typical pattern indicated the semi-crystalline nature of polymer gel electrolytes. The sharpness of the peaks increases with increase in O/Na ratio in PGE, which indicates that when we increase the 0/Na ratio crystallinity increases. We also calculated Interchain spacing (R') and inter- planar spacing (d) by these following formulas

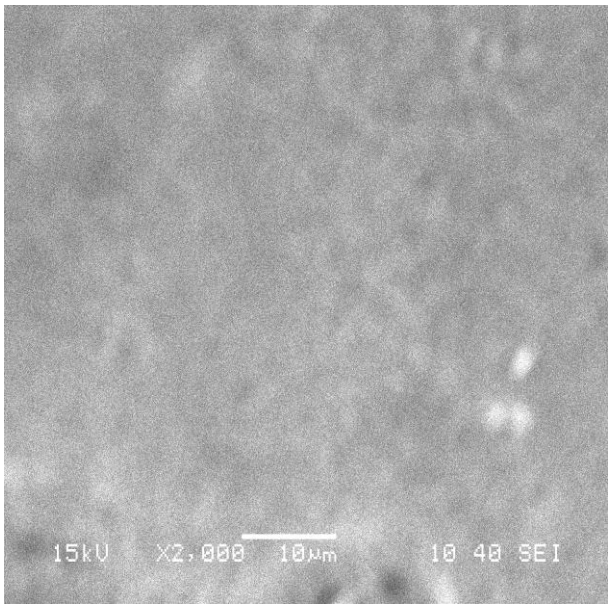
$$R' = \frac{7 \times \lambda}{2\pi\ 2sin\theta} \qquad \text{and} \qquad d = \frac{\lambda}{2sin\theta}$$

Table-2 Variation of interchain separation and interplanar spacing for different O/Na ratio.

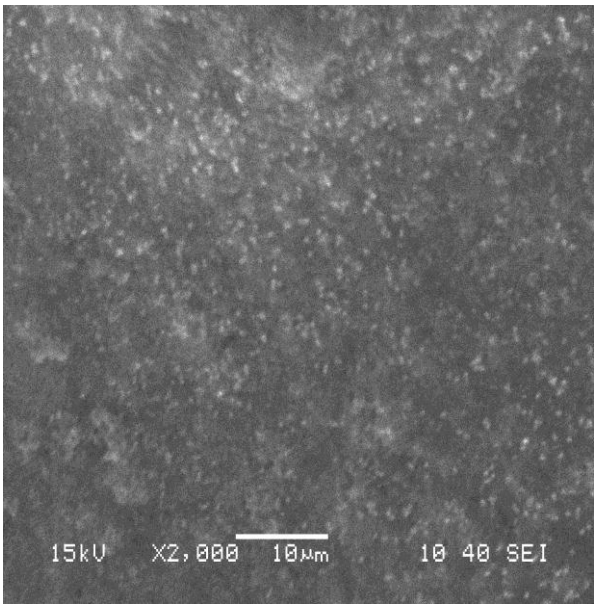
O/Na	2θ	FWHM	$R'(A^0)$	d
20	20.62	0.673 3	4.7924	4.3016
40	20.79	1.3843	4.7561	4.2691
60	20.39	1.2113	4.8465	4.3502
80	20.44	1.3380	4.8362	4.3409
100	20.40	1.3617	4.8452	4.3490

From this table we found that both Interchain separation and interplanar spacing increases with increase in O/Na ratio.

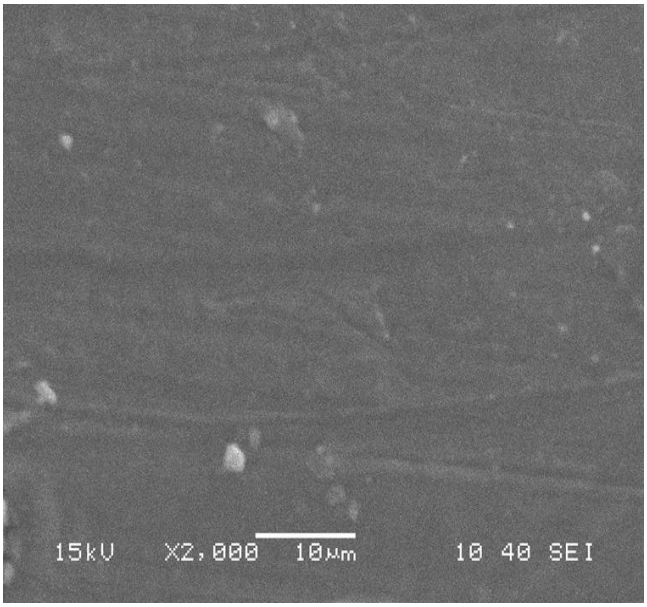
3.2. Scanning electron microscope



(a) O/Na=40



(b) O/Na=60



(c)O/Na=100 **Fig 3.2**

Fig. 3.2 shows the scanning electron micrographs of PGE with O/Na ratio i.e. 40, 60, 100. These figure shows that the crystallinity is increasing with increase in O/Na ratio and amount of amorphous content is decreasing. In the last composition i.e. O/Na=100 the amount of crystallinity is highest. The SEM micrographs confirm the results obtained in XRD**.**

3.3. DIELECTRIC SPECTROSCOPY

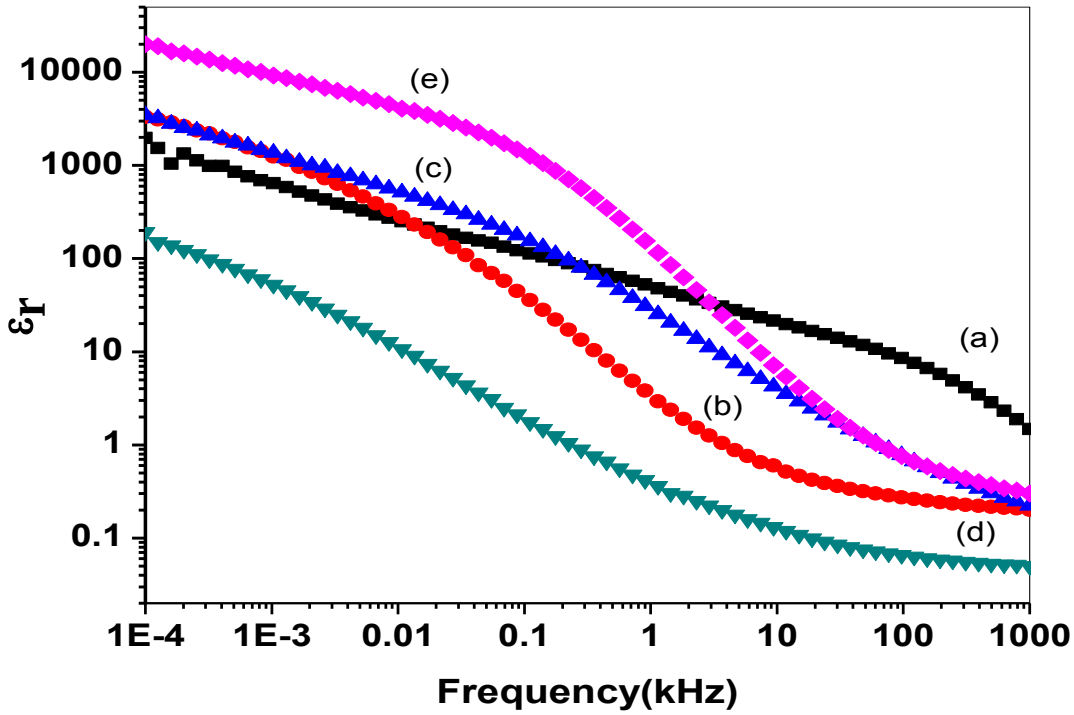


Fig.3.3.1. Dielectric constant versus frequency of PGE with different compositions

Dielectric constant versus frequency graphs for polymer gel electrolyte with different O/Na ratio is shown in Fig.3.3.1. In this figure we found that dielectric constant has higher value at lower frequency but when frequency increases dielectric constant decreases. The decrease of dielectric constant with increase in frequency is due to the relaxation phenomena but at the same time the effect of electrode polarization effect cannot be ignored at the low frequency range as the material are ionic conductors. Dielectric constant also increases with increase in O/Na ratio and the maximum value of dielectric constant was found for O/Na=100 at lower frequency.

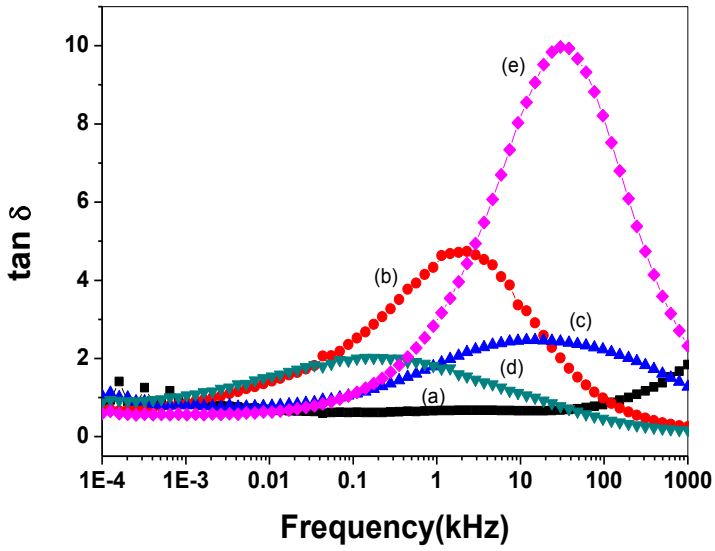


Fig 3.3.2.: $tan\delta$ versus Frequency of PGE with different O/Na composition

Fig.3.3.2 shows the $tan\delta$ versus Frequency of PGE with O/Na: 20, 40, 60, 80, and 100. In this fig. we found that when frequency increases $tan\delta$ increases and at a certain frequency it will become maximum and then with increase in frequency $tan\delta$ decreases. The $tan\delta$ peak has highest value for O/Na ratio=100. The appearance of peak $tan\delta$ versus Frequency plot suggests the presence of relaxing dipoles irrespective of different concentration.

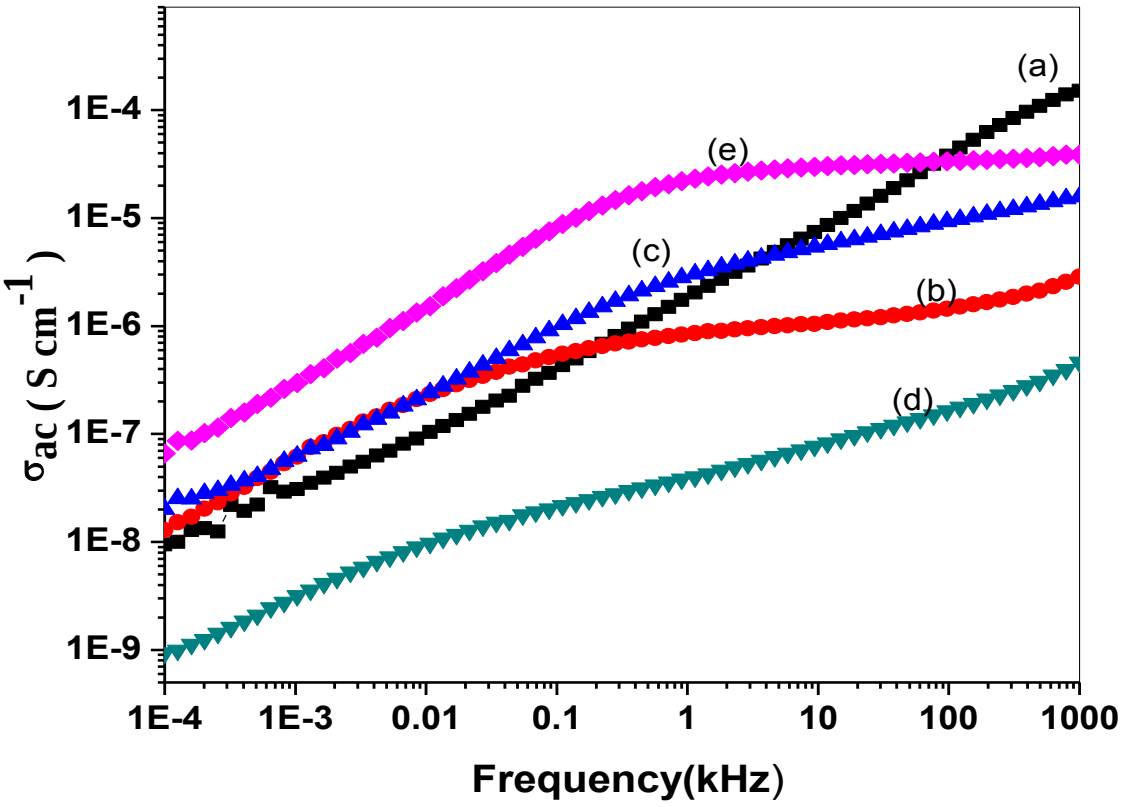
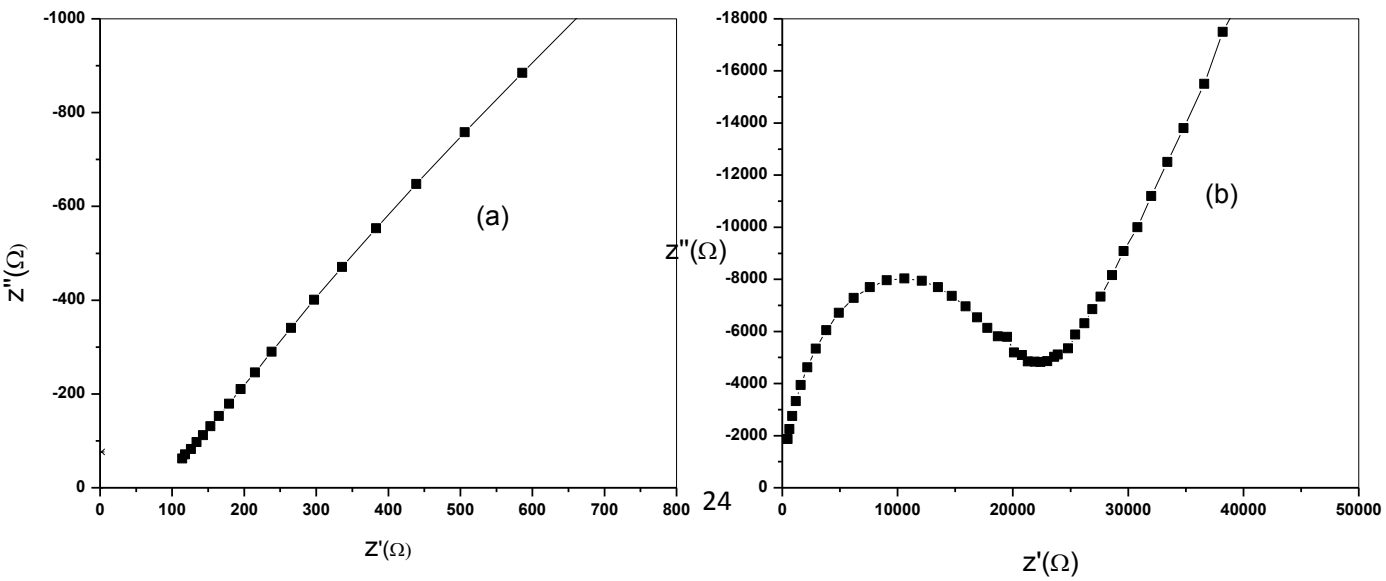


Fig 3.3.3 σ_{ac} versus frequency of PGE with O/Na=20, 40, 60, 80, 100

Fig.3.3.3 shows the variation σ_{ac} with frequency of PGE with different O/Na ratios. From this figure we found that at low frequency region when frequency increases σ_{ac} increases linearly for all composition but at higher frequency region σ_{ac} remains constant i.e. frequency independent. The observed frequency independent conductivity at higher frequency region is called d.c. conductivity.



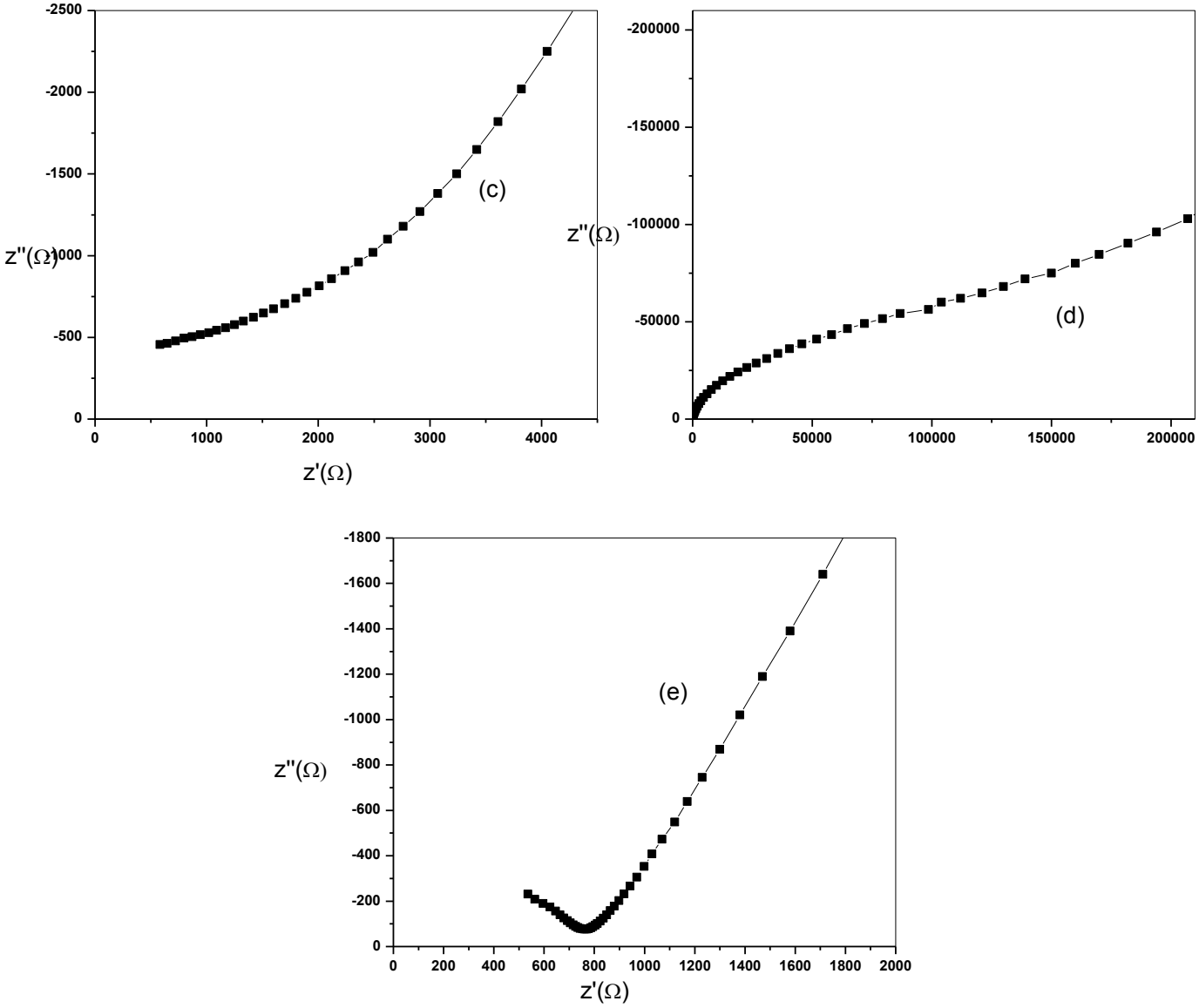


Fig 3.3.4 Z'' versus Z' of PGE

Fig. 3.3.4 shows the variation of Z'' with Z' for different O/Na ratio of PGE. In each figure there is a semi-circular arc at the high frequency region and a spike in the low frequency region. The semi-circular arc is formed due to bulk resistance whereas spike is formed due to metal electro interface. The intercept of the semi-circular arc on the real axis give the bulk resistance and from the bulk resistance we have calculated the dc conductivity using the following relation:

$$\sigma_{dc} = \frac{1}{R_b} \times \frac{l}{A}$$

Where R_b is the bulk resistance, l is the thickness of the sample, A is the area of the sample

Table-3 Calculated d.c. conductivity with different O/Na ratio:

O/Na	D.C. CONDUCTIVITY(σ_{dc}) (in S/cm)
20	5.6 X 10 $^{-4}$
40	2.2 X 10 -6
60	3.5 X 10 -5
80	6.1 X 10 -7
100	8.2 X 10 -5

From this table we found that dc conductivity of polymer gel electrolyte is varying from of the order of 10^{-4} to 10^{-7} S/cm and the maximum conductivity was found for O/Na=20.

CHAPTER-4

Summary and conclusion

A series of polymer gel electrolyte is synthesized using gelation method taking PVDF as polymer DMF as solvent and sodium iodide as salt. After synthesis it is characterized with different experimental techniques. For structural property we used XRD, for surface morphology we used SEM and for electrical properties we used dielectric spectroscopy. The main conclusions drawn from the result obtained is given below:

- From XRD, we found the (i) semi crystalline nature of PGEs and (ii) as the sharpness of the peak increases with increase in O/Na ratio, it indicates that crystallinity increases with increase in O/Na ratio.
- From SEM images we also found the same result as that obtained from XRD i.e., when O/Na ratio increases crystallinity increases.
- In dielectric study we plot dielectric constant vs. frequency, $tan\delta$ vs frequency, $\sigma_{ac}\ vs\ frequency,\ Z''$ and $Z',\ \sigma_{dc}$ vs frequency graphs.
- From these figures we found that dielectric constant of polymer gel electrolyte with increase in frequency irrespective of O/Na ratio.
- We calculated the σ_{dc} from complex impedance plot, which is of the order of 1.0×10^{-4} S/cm. The maximum conductivity was found for O/Na=20.

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